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**(54) Chromium catalyst compositions**

Chromkatalysatorzusammensetzungen

Composition de catalyseur à base de chrome

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## Description

BACKGROUND OF THE INVENTION

This invention is related to the field of chromium catalyst compositions.

It is known in the art that as the density of a polyolefin composition increases, the chemical resistance, tensile strength, and stiffness increase, but the permeability, toughness, and environmental stress crack resistance decrease. This can present a problem for example, when both a high density and a high environmental stress crack resistance are desired.

This invention provides a solution to this problem of competing performance factors.

EP-A-0 291 824 discloses chromium catalyst compositions comprising two supported chromium catalyst systems, wherein the support of one catalyst component has a pore volume greater than  $2 \text{ cm}^3/\text{g}$  and the support of the other catalyst component has a pore volume of  $1.5$  to  $1.9 \text{ cm}^3/\text{g}$ . Both catalyst components have chromium on a silica support, wherein one of the catalyst components also has aluminum deposited thereon.

SUMMARY OF THE INVENTION

It is an object of this invention to provide chromium catalyst compositions.

It is another object of this invention to provide chromium catalyst compositions useful in polymerizing olefins.

It is another object of this invention to provide chromium catalyst compositions useful in polymerizing ethylene.

It is another object of this invention to provide chromium catalyst compositions useful in copolymerizing ethylene and at least one other olefin.

It is another object of this invention to provide chromium catalyst compositions useful in copolymerizing ethylene and 1-hexene.

In accordance with this invention chromium catalyst compositions are provided as defined in claim 1. These chromium catalyst compositions comprise at least two chromium catalyst systems. These chromium catalyst systems comprise chromium and a support, wherein the support comprises silica, and wherein

(a) at least one of these chromium catalyst systems comprises chromium and a support,

wherein the support consists essentially of silica and titania, and wherein the support has an average pore radius less than  $8.5 \text{ nm}$  ( $85 \text{ angstroms}$ ), and wherein the support has a pore volume less than  $1.2 \text{ cm}^3$  per gram, and

wherein this chromium catalyst system is subjected to at least one of the following treatments (1) reduced and reoxidized, and (2) activated at a temperature greater than  $700^\circ\text{C}$ ;

(b) at least one of these chromium catalyst systems comprises chromium and a support,

wherein the support consists essentially of silica, and wherein the support has an average pore radius greater than  $8.5 \text{ nm}$  ( $85 \text{ angstroms}$ ), and wherein the support has a pore volume greater than  $1.5 \text{ cm}^3$  per gram, and

wherein this chromium catalyst system is subjected to at least one of the following treatments (1) activated at a low temperature less than  $700^\circ\text{C}$ , and (2) contacted with a fluorine compound.

In accordance with another embodiment of this invention, a process as defined in claim 1 is defined. In this process a chromium catalyst composition according to the invention is contacted with one or more different olefins, under polymerization conditions, to produce a polymer or copolymer.

This invention as disclosed in this application can be suitably practiced in the absence of any steps, components, compounds, or ingredients not disclosed herein.

DETAILED DESCRIPTION OF THE INVENTION

In general, the chromium catalyst compositions used in this invention comprise at least two chromium catalyst systems. These chromium catalyst systems comprise a chromium component and a support component comprising silica. The term "support component" is not meant to be construed as an inert component of the chromium catalyst system.

The supports used in the chromium catalyst systems of this invention can:

(1) comprise silicas

(2) consist essentially of silica and titania; or

(3) consist essentially of silica.

These supports are known in the art and are disclosed in U.S. Patents 2,825,721; 3,225,023; 3,226,205;

3,622,521; 3,625,864; 3,780,011; 3,887,494; 3,900,457; 3,947,433; 4,053,436; 4,081,407; 4,151,122; 4,177,162; 4,294,724; 4,296,001; 4,392,990; 4,402,864; 4,405,501; 4,434,243; 4,454,557; 4,735,931; 4,981,831; 5,037,911; the entire disclosures of which are hereby incorporated by reference. However, it should also be noted that these types of supports are available commercially from such sources as the Davison Chemical Division of the W. R. Grace Corporation.

The amount of silica present in the support is generally greater than 80 weight percent where the weight percent is based on the weight of the support. However, it is preferred that the amount of silica in the support is from 90 to 100 weight percent. The remaining portion, if any, can be selected from alumina, titania, boria, magnesia, thoria, zirconia, and mixtures of two or more thereof.

When the support consists essentially of silica and titania, the amount of silica in the support is generally greater than 80 weight percent where the weight percent is based on the weight of the support. However, it is also preferred that the amount of titania used in the support be greater than 0.1 weight percent. It is more preferred that the amount of titania used is from 1 weight percent to 20 weight percent and it is most preferred that the amount be from 1 weight percent to 10 weight percent.

The average pore radius of each support can be determined by nitrogen sorption by a person with ordinary skill in the art. For example, the following references can be used "Adsorption, Surface Area and Porosity" by S. J. Gregg and K. S. W. Sing, Academic Press, London (1982); and "Introduction to Powder Surface Area" by S. Lowell, J. Wiley & Sons, New York, NY (1979); the entire disclosures of which are hereby incorporated by reference.

The average pore radius may be calculated using the following formula:

$$\text{average pore radius in nm} = (4 \times 10^3) \frac{\text{pore volume in cm}^3 \text{ per gram}}{\text{surface area in m}^2 \text{ per gram}}$$

According to this invention the chromium catalyst compositions comprise at least two chromium catalyst systems. One of these chromium catalyst systems comprises chromium and a support wherein the support consists essentially of silica and titania. Another of these chromium catalyst systems comprises chromium and a support wherein the support consists essentially of silica.

The supports used according to the invention are further described as follows:

(1) the supports that consist essentially of silica and titania should have an average pore radius less than 8.5 nm (85 angstroms); however, it is preferred that they have an average pore radius from 2.5 to 8.5 nm (25 to 85 angstroms) and it is most preferred that they have an average pore radius from 3 to 8 nm (30 to 80 angstroms);

furthermore, the supports that consist essentially of silica and titania should have a pore volume less than 1.2 cm<sup>3</sup> per gram; however, it is preferred that they have a pore volume from 0.6 to 1.2 cm<sup>3</sup> per gram and it is most preferred that they have a pore volume from 0.8 to 1.15 cm<sup>3</sup> per gram; hereafter, these types of supports will be referred to as "type A supports";

(2) the supports that consist essentially of silica should have an average pore radius greater than 8.5 nm (85 angstroms); however, it is preferred that they have an average pore radius from 8.5 to 100 nm (85 to 1000 angstroms) and it is most preferred that they have an average pore radius from 9 to 50 nm (90 to 500 angstroms);

furthermore, the supports that consist essentially of silica should have a pore volume greater than 1.5 cm<sup>3</sup> per gram; however, it is preferred that they have a pore volume from 1.5 to 4 cm<sup>3</sup> per gram and it is most preferred that they have a pore volume from 1.5 to 3 cm<sup>3</sup> per gram; hereafter, these types of supports will be referred to as "type B supports."

The chromium component of the chromium catalyst systems that are part of the chromium catalyst compositions of this invention can be any suitable chromium compound that facilitates the polymerization of olefins. Suitable examples of chromium compounds included, but are not limited to, chromium nitrate, chromium acetate, chromium trioxide, and mixtures of two or more said chromium compounds. The amount of chromium compound that is combined with the support is from 0.1 weight percent to 5 weight percent. It is preferred that the amount be from 0.2 weight percent to 5 weight percent and it is most preferred that the amount be from 0.5 to 2 weight percent where the weight percent is based on the weight of the chromium compound and the support.

The chromium compound can be combined with the support in any manner known in the art. Examples of combining the chromium compound with the support can be found in the above cited and incorporated patents. Preferred methods of combining the chromium compound with the support are disclosed in U.S. Patents 3,976,632; 4,248,735; 4,297,460; and 4,397,766; the entire disclosures of which are hereby incorporated by reference. These patents disclose impreg-

nating the support with anhydrous chromium compounds.

According to this invention, chromium catalyst systems that comprise chromium and "type A supports" are (1) reduced and reoxidized, and (2) activated at a high temperature. Additionally, chromium catalyst systems that comprise chromium and "type B supports" are (1) activated at a low temperature, and (2) contacted with a fluorine compound. At least a portion of the chromium used in the invention is preferably in the hexavalent state.

The chromium catalyst systems used in this invention can be reduced and reoxidized in accordance with any manner known in the art that will reduce at least a portion of the chromium to a lower valence state and then reoxidized at least a portion of the chromium to a higher valence state. Suitable examples of this type of procedure can be found in U.S. Patents 4,151,122 and 4,177,162 the entire disclosures of which are hereby incorporated by reference.

The chromium catalyst systems used in this invention can be titanated in accordance with any manner known in the art that will combine a titanium compound with the chromium catalyst system. Suitable examples of this type of procedure can be found in U.S. Patents 3,622,521; 3,625,864; 3,780,011; 4,368,303; 4,402,864; 4,424,320; and 4,429,724; 4,434,243; the entire disclosures of which are hereby incorporated by reference.

The chromium catalyst systems used in this invention can be reduced in accordance with any manner known in the art that will reduce at least a portion of the chromium to a lower valence state. Suitable examples of this type of procedure can be found in U.S. Patent 4,735,931 the entire disclosure of which is hereby incorporated by reference. It is preferred that the reducing composition be carbon monoxide.

The chromium catalyst systems used in this invention can be contacted with a fluorine compound in accordance with any manner known in the art that will incorporate fluorine onto or into the chromium catalyst system. Suitable examples of this type of procedure can be found in U.S. Patents 2,825,721; 4,806,513; and 5,037,911; the entire disclosures of which are hereby incorporated by reference.

The chromium catalyst systems used in this invention can be activated in accordance with any manner known in the art that will contact an oxygen containing ambient with a chromium catalyst system. Suitable examples of this type of procedure can be found in U.S. Patents 3,887,494; 3,900,457; 4,053,436; 4,081,407; 4,296,001; 4,392,990; 4,405,501; 4,981,831; the entire disclosures of which are hereby incorporated by reference.

In general, activation at high temperature is conducted at a temperature greater than 700 °C and activation at low temperature is conducted at a temperature less than 700 °C. However, it is preferred that activation at a high temperature be conducted at a temperature between 750 and 900 °C; and most preferably it is conducted at a temperature between 800 and 900 °C. It is also preferred that activation at a low temperature be conducted at a temperature between 450 and 700 °C; and most preferably it is conducted at a temperature between 500 and 650 °C.

Once the chromium catalyst systems are made they may be combined together in any manner known in the art. For example, they can be dry blended together in a mixer or added to a feed stream that leads to a reactor. It is important to note that by varying the amounts of each chromium catalyst system included in the chromium catalyst composition, it is possible to vary the amount of comonomer incorporated into the resulting copolymer composition. Furthermore, by varying the amount of each chromium catalyst system included in the chromium catalyst composition, the density of the resulting polymer can be modified more independently of the melt index than was previously known for these types of chromium catalyst systems. Additionally, by varying the amount of each chromium catalyst system included in the chromium catalyst composition, or by varying the average pore radius difference between the supports in the chromium catalyst compositions, it is possible to preferentially introduce a non-ethylene comonomer into the higher molecular weight portion of a resulting copolymer. In general, the higher molecular weight portion can be determined using data collected by gel permeation chromatography using equipment readily available from commercial sources. The higher molecular weight portion is that portion greater than the weight average molecular weight. Preferentially introducing a non-ethylene comonomer into the higher molecular weight portion of a resulting copolymer means that a major portion of the comonomer is located in the higher molecular weight portion. This can be determined by calculating the number of short chain alkyl branches in the polymer. For example, in an ethylene and 1-hexene copolymer the number of butyl branches will give an indication of the amount of 1-hexene comonomer incorporated into the polymer.

The chromium catalyst compositions used in this invention can be contacted with one or more olefins under polymerization conditions to produce homopolymer or copolymer compositions. Suitable olefins include, but are not limited to, ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene and mixtures of two or more of said olefins. Particularly preferred is ethylene. Additionally, a particularly preferred combination of olefins to use is ethylene and 1-hexene. These two olefins are particularly preferred at this time because these olefins copolymerized especially well with the chromium catalyst compositions disclosed in this invention.

Various polymerization schemes are known in the art. For example, U.S. Patents 2,825,721; 3,152,872; 3,172,737; 3,203,766; 3,225,023; 3,226,205; 3,242,150; 3,248,179; and 4,121,029; (the entire disclosures of which are hereby incorporated by reference) disclose several polymerization schemes. A particularly preferred polymerization method is a slurry or particle form polymerization method. This method is disclosed for example, in U.S. Patent 3,248,179. Two preferred slurry polymerization techniques are those employing a loop reactor and those employing a plurality of stirred

reactors either in series, parallel or combinations thereof.

## Claims

- 5 1. A chromium catalyst composition that comprises at least two chromium catalyst systems, wherein said chromium catalyst systems comprise chromium and a support, wherein the support comprises silica, wherein
  - (a) at least one of said chromium catalyst systems comprises chromium and a support, wherein the support consists essentially of silica and titania, and wherein the support has an average pore radius less than 8.5 nm (85 angstroms), and wherein the support has a pore volume less than 1.2 cm<sup>3</sup> per gram, and wherein this chromium catalyst system is subjected to at least one of the following treatments (1) reduced and reoxidized, and (2) activated at a temperature greater than 700 °C;
  - 10 (b) at least one of said chromium catalyst systems comprises chromium and a support, wherein the support consists essentially of silica, and wherein the support has an average pore radius greater than 8.5 nm (85 angstroms), and wherein the support has a pore volume greater than 1.5 cm<sup>3</sup> per gram, and wherein this chromium catalyst system is subjected to at least one of the following treatments (1) activated at a temperature less than 700 °C, and (2) contacted with a fluorine compound.
- 20 2. The chromium catalyst composition of claim 1 wherein said silica-titania support has an average pore radius from 2.5 to 8.5 nm (25 to 85 angstroms), preferably from 3 to 8 nm (30 to 80 angstroms).
3. The chromium catalyst composition of claim 1 or 2 wherein said silica-titania support has a pore volume from 0.6 to 1.2 cm<sup>3</sup> per gram, preferably from 0.8 to 1.15 cm<sup>3</sup> per gram.
- 25 4. The chromium catalyst composition of any of claims 1 to 3 wherein said silica support has an average pore radius from 8.5 to 100 nm (85 to 1000 angstroms), preferably from 9 to 50 nm (90 to 500 angstroms).
5. The chromium catalyst composition of any of claims 1 to 4 wherein said silica support has a pore volume from 1.5 to 4 cm<sup>3</sup> per gram, preferably from 1.5 to 3 cm<sup>3</sup> per gram.
- 30 6. The chromium catalyst composition of any of claims 1 to 5 wherein said silica-titania support consists essentially of at least 80 weight percent silica and at least 0.1 weight percent titania, preferably at least 90 weight percent silica and at least 1 weight percent titania, where the weight percent is based on the weight of the support.
- 35 7. The chromium catalyst composition of any of the preceding claims wherein said chromium is present in said chromium catalyst systems in an amount from 0.1 to 5 weight percent.
8. A process of polymerizing at least one type of olefin with a chromium catalyst composition of any of the preceding claims.
- 40 9. The process of claim 8 wherein said olefin is selected from ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene, and mixtures of two or more said olefins.
- 45 10. The process of claim 8 or 9 wherein said olefin is ethylene and 1-hexene.

## Patentansprüche

- 50 1. Chromkatalysatorzusammensetzung, die mindestens zwei Chromkatalysatorsysteme umfaßt, wobei die Chromkatalysatorsysteme Chrom und einen Träger umfassen, wobei der Träger Siliciumdioxid umfaßt, wobei
  - (a) mindestens eines der Chromkatalysatorsysteme Chrom und einen Träger umfaßt, wobei der Träger im wesentlichen aus Siliciumdioxid und Titandioxid besteht und wobei der Träger einen mittleren Porenradius von weniger als 8,5 nm (85 Å) aufweist und wobei der Träger ein Porenvolumen von weniger als 1,2 cm<sup>3</sup> pro g aufweist und wobei dieses Chromkatalysatorsystem mindestens einer der folgenden Behandlungen unterzogen wird: (1) Reduktion und Wiederoxidation und (2) Aktivierung bei einer Temperatur von mehr als 700 °C;
  - 55 (b) mindestens eines der Chromkatalysatorsysteme Chrom und einen Träger umfaßt, wobei der Träger im wesentlichen aus Siliciumdioxid besteht und wobei der Träger einen mittleren Porenradius von mehr als 8,5 nm

(85 Å) aufweist und wobei der Träger ein Porenvolumen von mehr als  $1,5 \text{ cm}^3$  pro g aufweist und wobei dieses Chromkatalysatorsystem mindestens einer der folgenden Behandlungen unterzogen wird: (1) Aktivierung bei einer Temperatur von weniger als  $700^\circ\text{C}$  und (2) Kontaktieren mit einer Fluorverbindung.

- 5 2. Chromkatalysatorzusammensetzung nach Anspruch 1, wobei der Siliciumdioxid-Titandioxid-Träger einen mittleren Porenradius von 2,5 bis 8,5 nm (25 bis 85 Å) und vorzugsweise von 3 bis 8 nm (30 bis 80 Å) aufweist.
3. Chromkatalysatorzusammensetzung nach Anspruch 1 oder 2, wobei der Siliciumdioxid-Titandioxid-Träger ein Porenvolumen von 0,6 bis  $1,2 \text{ cm}^3$  pro g und vorzugsweise von 0,8 bis  $1,15 \text{ cm}^3$  pro g aufweist.
- 10 4. Chromkatalysatorzusammensetzung nach einem der Ansprüche 1 bis 3, wobei der Siliciumdioxidträger einen mittleren Porenradius von 8,5 bis 100 nm (85 bis 1000 Å) und vorzugsweise von 9 bis 50 nm (90 bis 500 Å) aufweist.
- 15 5. Chromkatalysatorzusammensetzung nach einem der Ansprüche 1 bis 4, wobei der Siliciumdioxidträger ein Porenvolumen von 1,5 bis  $4 \text{ cm}^3$  pro g und vorzugsweise von 1,5 bis  $3 \text{ cm}^3$  pro g aufweist.
- 20 6. Chromkatalysatorzusammensetzung nach einem der Ansprüche 1 bis 5, wobei der Siliciumdioxid-Titandioxid-Träger im wesentlichen aus mindestens 80 Gew.-% Siliciumdioxid und mindestens 0,1 Gew.-% Titandioxid und vorzugsweise aus mindestens 90 Gew.-% Siliciumdioxid und mindestens 1 Gew.-% Titandioxid besteht, wobei der Gewichtsprozentsatz sich auf das Gewicht des Trägers bezieht.
7. Chromkatalysatorzusammensetzung nach einem der vorstehenden Ansprüche, wobei das Chrom in den Chromkatalysatorsystemen in einer Menge von 0,1 bis 5 Gew.-% vorhanden ist.
- 25 8. Verfahren zur Polymerisation mindestens einer Art von Olefin mit einer Chromkatalysatorzusammensetzung nach einem der vorstehenden Ansprüche.
9. Verfahren nach Anspruch 8, wobei das Olefin unter Ethylen, Propylen, 1-Buten, 3-Methyl-1-buten, 1-Penten, 3-Methyl-1-penten, 4-Methyl-1-penten, 1-Hexen, 3-Ethyl-1-hexen, 1-Octen, 1-Decen und Gemischen von zwei oder
- 30 mehr dieser Olefine ausgewählt ist.
10. Verfahren nach Anspruch 8 oder 9, wobei es sich bei dem Olefin um Ethylen und 1-Hexen handelt.

#### Revendications

- 35 1. Une composition de catalyseur de chrome qui comprend au moins deux systèmes de catalyseurs de chrome où lesdits systèmes de catalyseurs de chrome renferment du chrome et un support, où le support comprend de la silice, dans laquelle:
  - 40 (a) au moins l'un desdits systèmes de catalyseurs de chrome comprend du chrome et un support où le support se compose essentiellement de silice et d'oxyde de titane et où le support a un rayon de pores moyen inférieur à 8,5 nm (85 angströms), et où le support a un volume de pores inférieur à  $1,2 \text{ cm}^3/\text{g}$  et où ce système de catalyseur de chrome est soumis à au moins l'un des traitements suivants (1) une réduction et une réoxydation et, (2) une activation à une température supérieure à  $700^\circ\text{C}$ ;
  - 45 (b) au moins l'un desdits systèmes de catalyseurs de chrome renferme du chrome et un support où le support se compose essentiellement de silice et où le support a un rayon de pores moyen supérieur à 8,5 nm (85 angströms) et où le support a un volume de pores supérieur à  $1,5 \text{ cm}^3/\text{g}$  et où ce système de catalyseur de chrome est soumis à au moins l'un des traitements suivants (1) une activation à une température inférieure à  $700^\circ\text{C}$  et (2) une mise en contact avec un composé de fluor.
- 50 2. La composition de catalyseur de chrome selon la revendication 1, dans laquelle ledit support de silice-oxyde de titane a un rayon de pores moyen de 2,5 à 8,5 nm (25 à 85 angströms), de préférence de 3 à 8 nm (30 à 80 angströms).
- 55 3. La composition de catalyseur de chrome selon la revendication 1 ou 2, dans laquelle ledit support de silice-oxyde de titane a un volume de pores de 0,6 à  $1,2 \text{ cm}^3/\text{g}$ , de préférence de 0,8 à  $1,15 \text{ cm}^3/\text{g}$ .
4. La composition de catalyseur de chrome selon l'une quelconque des revendications 1 à 3, dans laquelle ledit support de silice a un rayon de pores moyen de 8,5 à 100 nm (85 à 1000 angströms) de préférence de 9 à 50 nm (90

à 500 angströms).

- 5 5. La composition de catalyseur de chrome selon l'une quelconque des revendications 1 à 4, dans laquelle ledit support de silice a un volume de pores de 1,5 à 4 cm<sup>3</sup>/g, de préférence de 1,5 à 3 cm<sup>3</sup>/g.
6. La composition de catalyseur de chrome selon l'une quelconque des revendications 1 à 5, dans laquelle ledit support de silice-oxyde de titane se compose essentiellement d'au moins 80% en poids de silice et d'au moins 0,1% en poids d'oxyde de titane, de préférence, d'au moins 90% en poids de silice et d'au moins 1% en poids d'oxyde de titane où les pourcentages en poids sont basés sur le poids du support.
- 10 7. La composition de catalyseur de chrome selon l'une quelconque des revendications précédentes, dans laquelle ledit chrome est présent dans lesdits systèmes de catalyseurs de chrome selon une quantité de 0,1 à 5% en poids.
8. Un procédé de polymérisation d'au moins un type d'oléfine avec une composition de catalyseur de chrome selon l'une quelconque des revendications précédentes.
- 15 9. Un procédé selon la revendication 8, dans lequel ladite oléfine est choisie parmi l'éthylène, le propylène, le 1-butène, le 3-méthyl-1-butène, le 1-pentène, le 3-méthyl-1-pentène, le 4-méthyl-1-pentène, le 1-hexène, le 3-éthyl-1-hexène, le 1-octène, le 1-décène et un mélange de deux ou plusieurs desdites oléfines.
- 20 10. Le procédé selon la revendication 8 ou 9, dans lequel ladite oléfine est l'éthylène et le 1-hexène.